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# Adsorption of lead ions from an aqueous solution onto NaOH-modified rice husk

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## ABSTRACT

In the current study, the adsorption of toxic lead ions from aqueous solution by NaOH-modified rice husk (MRH) was investigated. The effect of operating factors such as contact time, amount of MRH (adsorbent), initial concentration of metal ions (lead ions) in aqueous solution, temperature and initial solution pH on the adsorptive removal of lead ions from aqueous solution by using MRH was considered. The adsorption results demonstrated that the percentage removal of lead ions was increased with contact time, mass of MRH and pH while declined with initial concentration of lead ions and temperature. Adsorption of lead ions onto MRH was subjected to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. Results represented that adsorption of lead ions fitted well to Langmuir isotherm indicating that surface adsorption and monolayer coverage of lead ions onto MRH surface. The maximum Langmuir adsorption capacity was 28.6 mg/g. The kinetic study illustrated those lead ions adsorption onto MRH was fitted to pseudo-second-order kinetic model. The thermodynamic parameters investigations revealed that lead ions removal by MRH was an exothermic and spontaneous adsorption process. The MRH demonstrated more than 75% removal of lead ions after 4 adsorption/desorption cycles. Therefore, MRH could be utilized as an extraordinary adsorbent for removal of lead ions from aqueous solution.

*Keywords:* Lead ions; Adsorption isotherm; Water treatment; Exothermic reaction; Rice husk

## 1. Introduction

In the aquatic environmental, the existence of heavy metals has been a big deal to engineers and scientists because they are non-biodegradable, toxic in nature, and other adverse effects on receiving waters [1,2]. Nowadays, it is still possible to find some heavy metal ions in the wastewater due to industrial processes inspite of the strict regulations on environmental issues imposed in several countries [3,4]. However, when such polluted water is unconsciously discharged into natural water flows, it resulted to true environmental damage. Moreover, the human health is also at risk in addition to aquatic animals and plants [5–7].

Heavy metals including chromium, lead, copper, zinc, cadmium, mercury, nickle, etc. present causes several environmental challenges according to their toxicity. Among heavy metals, Lead is one of the most dangerous metal for the human health, particularly for children due to the fact that, their growing bodies can absorb higher amounts of lead than adults [8–10]. Although lead is forbidden in several products, it is still employed in commercial products as automotive batteries, cookware, paints, and some Mexican potter glazes [11,12]. It also has applications in fuels, printing pigments manufacturing, photographic materials, and explosive manufacturing [13]. Human health is under the stress of increasing lead concentration in water bodies;

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several reports have stated that some not dangerous diseases including anemia, diarrhea, and headaches are seen at a low concentrations of lead ions in the blood, while, at a higher concentration (>10 μg/L), the liver, kidney, and neurological and reproductive systems can be seriously damaged [4,14]. Hence, the small concentration of lead is also very toxic for living organism and human being.

Several scientists tried to withdraw heavy metal from wastewater bodies. They utilized several conventional method including chemical precipitation [15], ion-exchange [16], floatation [17], coagulation [18], membrane processes [19], solvent extraction [20] and adsorption [21–23] to remove heavy metals from aqueous solutions. Among these employed procedures, adsorption is considered one of the most renowned methods to remove heavy metals. It represented many advantages including low cost, easy operation, high efficiency, and production of less sludge volume [24].

To date several types of materials such as activated carbons [25], carbon nanotubes [26], zeolites [27], chitosan [28], clays [29] and agricultural wastes [30] were utilized to remove metal cations from aqueous solutions. However, in the last few decades, researchers have been utilized the bio adsorbents for heavy metals remediation. Biosorbents including coconut shell, rice husks, wheat shell, sunflower stalk, soybean hulls, walnut shell, banana stalk, sugarcane bagasse and other agriculture products and plants wastes were used for the removal of organic and inorganic pollutants. Among them, the rice husk gained more attraction for the adsorption process since it has high mechanical strength, chemically stable, insoluble in water as well as cost effective material [31]. Moreover, rice is being cultivated in more than 75 countries (mainly in Asia) and the world consumption of rice is around 80 million tons annually [32]. Furthermore, the husk accounts almost 20%–23% of the rice plant [32]. And hence, due to its wide availability with no cost, rice husk is a potential adsorbent for several kinds of pollutants. For lead removal, it was reported that the maximum adsorption capacity of lead onto untreated grinded rice husk was 4 g per kg of rice husk (i.e., 4 mg/g) [33]. Later, Naiya et al. [34] has improved the capacity of lead onto rice husk waste by testing the removal of lead by rice husk ash and they obtained higher adsorption capacity. Recently, Shi et al. [35] prepared a rice husk biochar and tested its ability for lead ions adsorption. They obtained a maximum capacity of 26.7 mg/g for the rice husk biochar pyrolyzed at 700°C [35]. The main drawbacks of raw rice husk including low lead adsorption capacity as well as less selectivity [31]. Therefore, NaOH-treated rice husk could enhance he adsorption capacity by modifying the rice husk functional groups. The chemical treatment of bio sorbents by NaOH has proven its ability toward improving the removal of cationic pollutants. It was reported that NaOH treatment can alter the functional groups onto the surface of biosorbents by increasing the intensity of several groups such as C=O, C–H, and O–H which have resulted in increased ion exchange capacity with cationic pollutants [36,37]. Moreover, NaOH treatment can increase the ionic ligands of amino and carboxyl groups and resulted in increased electrostatic interaction forces [36,37]. For instance, the removal of lead has improved by NaOH treatment of rice bran and corncobs [36,37]. Moreover, the cationic copper ions removal has been improved by NaOH treatment of rice husk and pine cone powder [38,39]. To the best of our knowledge, the NaOH activation of rice husk for the removal of lead ions from aqueous solution is not reported yet.

Previously, we studied adsorption of heavy metal ions, and anionic dyes from aqueous solution onto rice husk, leaves powder of various plants [40–42], and ion exchange membrane [43–48]. The objectives of the current study; (i) investigate the potential adsorption of lead ions from aqueous solution onto modified rice husk (MRH). (ii) Investigating the effect of operating endowments including pH, adsorbent dosage, contact time, initial lead concentration, and temperature on the removal efficiency of lead ions. And finally, (iii) proposing the adsorption mechanism of lead ions onto modified rice husk by analyzing the isotherm, kinetic and thermodynamics data.

## 2. Experimental

### 2.1. Materials

Lead nitrate $Pb(NO_3)_2$ (purity: 99.5%), sodium hydroxide (NaOH) (purity: 99%), hydrochloric acid (HCl) (purity: 37%) were kindly supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the chemicals were utilized as received. Throughout this work, deionized water was utilized.

### 2.2. Adsorbent

Husk of basmati rice was kindly provided by the rice mill, Punjab, Pakistan. To withdraw dust particle, it was thoroughly washed with distilled water and oven dried at 80°C till constant weight was achieved. Neutron activation analysis (NAA) and atomic adsorption spectrometry (AAS) methods were utilized for its chemical analysis employing for their trace metal contents and achieved results were reported in our previous work [49,50]. It was noted that the quantity of metals such as Na, K, Pb and Fe were present in μg/g of sample. Silica contents were found to be 18.27 (0.62%) of MRH [50,51]. The small contents of elements in MRH was analysed via standard methods.

### 2.3. Modification of RH

For this purpose, the dried and cleaned RH was modified with 1.0 M NaOH solution. Initially, 50 g of RH was added in the NaOH solution into a 1.0 L beaker. The mixture was shaked vigorously for 24 h. After that, the RH was cleaned until neutral pH was obtained with distilled water. Then, it was dried in oven at 80°C till constant weight was obtained and stored in airtight container. It was denoted as MRH.

### 2.4. Adsorption of lead ions onto modified-RH

Adsorption of lead ions onto MRH was performed as described in our previous research [50–56]. A known quantity of MRH was taken into a 25 $cm^3$ secured cap culture tube along with 4 $cm^3$ of standard acid solution and a constant volume of stock radiotracer with known amount of lead ions concentration solution was added. Consecutively, the contents were equilibrated on a wrist-action mechanical shaker (Vibromatic, USA) at a rate of 500 rpm for specific intervals of time. Then, it was centrifuged at 5,000 rpm for phase separation and the supernatant solution was removed for activity measurement. The radioactivity of solutions before ($A_i$) and after ($A_f$) equilibrium was measured with a NaI well type scintillation counter (Canberra Inc.) coupled with a counter-scaler (Nuclear Chicago). A volume of 1.0 cm$^3$ was normally employed to record activity. All research was conducted at ambient temperature except where otherwise specified. The percentage removal of lead ions by using MRH from aqueous solution was calculated using Eq. (1):

$$\%\text{adsorption} = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

where $A_i$ and $A_f$ represent initial and final adsorption of lead ions (counts/min) into aqueous solution respectively.

## 2.5. Characterization

### 2.5.1. Brunauer–Emmett–Teller surface area

The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore diameter were evaluated by the nitrogen adsorption/desorption isotherm by using the BET analyzer (Type: Novatech LX2 analyzer, Anton Paar, Austria). The equipment was degassed at 300°C for 6 h before conducting the experiment.

### 2.5.2. Fourier-transform infrared spectroscopy test

Fourier-transform infrared spectroscopy (FTIR) spectrometer (Vector 22, Bruker) containing resolution of 2 cm$^{-1}$ and total spectral range of 4,000–400 cm$^{-1}$ was utilized to reveal MRH before and after lead ions adsorption onto it by utilizing attenuated total reflectance (ATR).

### 2.5.3. Morphological study

Surface morphology and elemental composition of rice husk before and after modification was studied by employing field-emission scanning electron microscope (FE-SEM, Apreo, Thermo Fisher Scientific, USA). The scanning electron microscopy (SEM) is operated with energy dispersive spectrometer (EDS, Bruker XFlash® 6-60, Germany) which was used for elemental chemical composition analysis.

### 2.5.4. Zero point of charge ($pH_{ZPC}$)

The zero point of charge ($pH_{ZPC}$) of MRH was evaluated by the pH drift method. Briefly, 20 mg of MRH was added to 20 mL of 0.1 M NaCl solutions. The initial pH ($pH_i$) of the NaCl solutions was adjusted between 2.1 and 11.2 by the addition of 0.1 M of HCl or NaOH. Next, the solutions were allowed for shaking for 72 h and the final pH ($pH_f$) was measured. The $pH_{ZPC}$ was calculated by plotting the $pH_i$ against the difference in the pH ($pH_f - pH_i$).

## 2.6. Effect of operating factors

The following sections (2.6.1–2.6.5) provide the detailed experimental conditions of the current study. The reasons behind selecting these conditions are explained in Section S1.

### 2.6.1. Effect of contact time

The influence of contact time on the removal of lead ions from aqueous solution was explored by keeping mass of MRH (0.025 g), initial concentration lead ion in aqueous (20 mg/L), volume of lead ion aqueous solution (20 mL), and stirring speed (200 rpm) constant at room temperature.

### 2.6.2. Effect of mass of MRH

The effect of mass of MRH on the removal of lead ions was studied by varying mass of MRH from 0.01 to 0.04 g keeping contact time (1,440 min), volume of lead ions aqueous solution (20 mL), initial concentration of lead ions in aqueous solution (30 mg/L), stirring speed (200 rpm) constant at room temperature.

### 2.6.3. Effect of initial concentration

It was investigated by changing initial concentration of lead ion in aqueous solution from 20 to 100 mg/L keeping mass of MRH (0.025 g), contact time (1,440 min), volume of lead ion aqueous solution (20 mL), and stirring speed (200 rpm) constant at room temperature.

### 2.6.4. Effect of temperature

It was revealed by varying temperature from 295 to 333 K keeping contact time (1,440 min), volume of lead ion aqueous solution (20 mL), mass of MRH (0.025 g), initial concentration of lead ion in aqueous solution (30 mg/L) and stirring speed constant (200 rmp) constant.

### 2.6.5. Effect of initial solution pH

It was evaluated by varying pH from 2.7 to 6.7 keeping initial concentration of lead ions in aqueous solution (30 mg/L), mass of MRH (0.025 g), volume of lead ion aqueous solution (20 mL), stirring speed (200 rpm) constant at room temperature.

## 2.7. Adsorption isotherms

Adsorption isotherms including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich were employed to explore experimental data for adsorption of lead ions from aqueous solution onto MRH.

### 2.7.1. Langmuir isotherm

It is based on the maximum adsorption corresponds to the saturated monolayer of liquid molecules on the solid surface. It is represented as follows [57–59].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (2)$$

where $K_L$ is Langmuir constant (L/mg) and $Q_m$ is Langmuir monolayers adsorption capacity (mg/g), $C_e$ is supernatant concentration at equilibrium state of the system (mg/L), and $q_e$ is the amount of dye adsorbed at equilibrium state of system (mg/g). The essential characteristics of Langmuir isotherm can be shown denoted in term of dimensionless constant separation factor $R_L$ that is given by [60].

$$R_L = \frac{1}{1 + K_L C_o} \tag{3}$$

The value of $R_L$ indicated the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L > 0$), or irreversible ($R_L = 0$) [61].

### 2.7.2. Freundlich isotherm

It is an empirical relation employed to explain the heterogeneous system. The Freundlich isotherm model is shown as [62].

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

where $K_f$ and $n_F$ are Freundlich constant.

### 2.7.3. Temkin isotherm

The linear form of Temkin isotherm is expressed as [42]:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{5}$$

where $B_T = RT/b_T$, $R$ is gas constant (8.31 J/mol K) and $T$ is absolute temperature (K). The constant $b_T$ is related to the heat of adsorption and $A_T$ is equilibrium binding constant coinciding to the maximum binding energy.

### 2.7.4. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich model is shown as [42]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{6}$$

where β (mol$^2$/KJ) is constant related to the adsorption energy and ε is the Polanyi potential can be determined by using below relationship.

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

where $R$ is gas constant (8.31 kJ/mol) and $T$ is absolute temperature (K). The mean free energy $E$ (kJ/mol) can be calculated by Eq. (8):

$$E = \frac{1}{\sqrt{2\beta}} \tag{8}$$

## 2.8. Adsorption kinetics

Adsorption kinetics for adsorption of lead ions from aqueous solution onto MRH was explored by using several kinetic models.

### 2.8.1. Pseudo-first-order model

The linear form of Lagergren pseudo-first-order rate in is given as [40,41,53,63]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1 t}{2.303} \tag{9}$$

where $K_1$ (min$^{-1}$), $q_e$ and $q_t$ shows rate constant of pseudo-first-order model, concentration of lead ions adsorbed at equilibrium and time $t$ respectively.

### 2.8.2. Pseudo-second-order model

The linear form of pseudo-second-order kinetic model is represented as [45,63]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where $K_2$ (g/mg min) is the rate constant of pseudo-second-order model.

### 2.8.3. Elovich model

The Elovich model is expressed as [44,64]:

$$q_t = \frac{1}{\beta}\ln\left(\alpha\beta\right) + \frac{1}{\beta}\ln t \tag{11}$$

where α (mg/g min) and β (g/mg) are constant. The parameter α is initial adsorption rate and β is the extent of surface coverage and activation energy for chemisorption.

### 2.8.4. Liquid film diffusion model

It is shown as [65]:

$$\ln\left(1 - F\right) = -K_{\text{fd}} t \tag{12}$$

where $K_{\text{fd}}$ is liquid film diffusion rate constant, and $F = q_t/q$.

### 2.8.5. Modified Freundlich equation

It was originally developed by Kuo and Lotse [45,66]:

$$q_t = kC_o t^{1/m} \tag{13}$$

where $k$, $C_o$, $t$ and $m$ are adsorption rate constant (L/g min), initial concentration (mg/L), contact time (min) and the Kuo–Lotse constant respectively. Its linear form is expressed as:

$$\ln q_t = \ln\left(kC_o\right) + \frac{1}{m}\ln t \tag{14}$$

### 2.8.6. Bangham equation

Bangham equation is represented as [63,64]:

$$\log\log\left(\frac{C_o}{C_o - q_t m}\right) = \log\left(\frac{k_o m}{2.303V}\right) + \alpha\log t \tag{15}$$

where $m$ is mass of the MRH (adsorbent) employed (g/L), $V$ is volume of lead ion aqueous solution (mL), α (<1) and $k_o$ (mL/(g/L)) are constants.

## 2.9. Thermodynamics study

For adsorption of lead ions from aqueous solution onto MRH, the change in Gibb's free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were calculated to investigate adsorption thermodynamics as described [44,63,64,67].

We calculated change in Gibb's free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were determined by using Eqs. (16)–(18):

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{16}$$

$$K_c = \frac{C_a}{C_e} \tag{17}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{18}$$

where $K_c$, $\Delta G°$, $\Delta H°$ and $\Delta S°$ are equilibrium constant, change in Gibb's free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively.

## 2.10. Regeneration/desorption experiments

Desorption experiments were conducted in batch mode at similar conditions (lead initial concentration 30 mg/L, 20 mL solution, 25 mg of MRH, agitation speed 200 rpm, as prepared pH 5.4 and room temperature). The spent MRH from the first experiments was separated by centrifugation and then washed with 0.1 M HCl for 4 h. Next, the MRH washed several times with DI until neutral pH is achieved and then, this adsorbent used for the next adsorption study.

# 3. Results and discussion

## 3.1. Morphology, energy-dispersive X-ray spectroscopy and surface area

Morphological features of non-modified and MRH were studied by using SEM. Fig. 1 depicts SEM micrograph of non-modified (Fig. 1a) and MRH (Fig. 1b). It was noted that the surface morphology of non-modified RH was rough. It was change to smooth after modification with NaOH. It was noted that MRH possess pores on it which are excellent for adsorption of lead ions from aqueous solution. After adsorption, no major changes occurred onto the surface of the MRH as seen in Fig. 1c.

The surface area, pore volume and pore diameter were evaluated by the BET analyzer. The nitrogen adsorption/desorption were evaluated by the Barrett, Joyner, and Halenda (BJH) method and the results are illustrated in Table 1. The MRH demonstrated a surface area of 5.42 m$^2$/g.

To confirm the removal of lead ions by MRH, the energy-dispersive X-ray spectroscopy (EDS) analysis were carried out for the raw MRH and the spent adsorbent and the results are illustrated in Fig. 2. As illustrated in Fig. 2a, the modified rice husk is mainly consisted of carbon, oxygen, silicon and traces of Ca, K, Mg, Al and P. and K (0.4 wt.%). After the lead ions removal (Fig. 2b), the elemental compositing has slightly changed due to location changes, however, the dominant elements are the

Table 1
Surface properties of MRH evaluated by the BET analyzer

| | |
|---|---|
| Surface area (m$^2$/g) | 5.42 |
| Pore volume (cc/g) | 0.018 |
| Pore diameter (nm) | 3.44 |

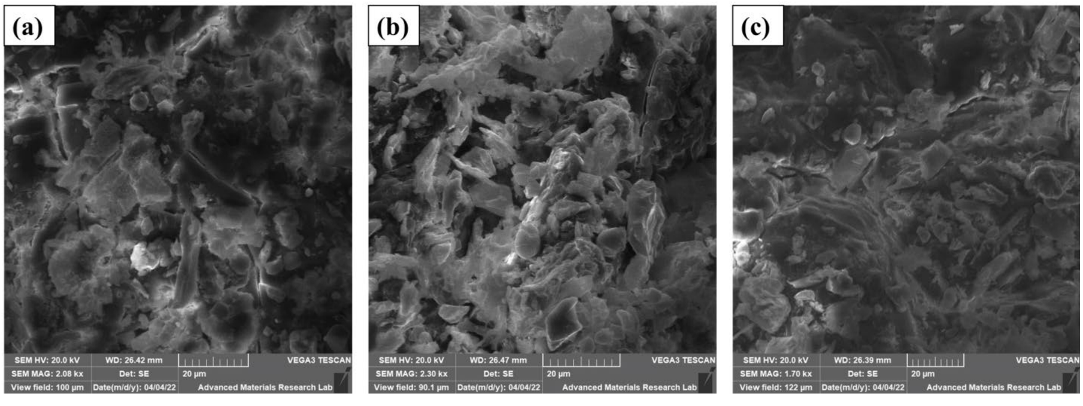


Fig. 1. SEM micrographs of (a) non-modified RH, (b) MRH, and (c) MRH after adsorption.

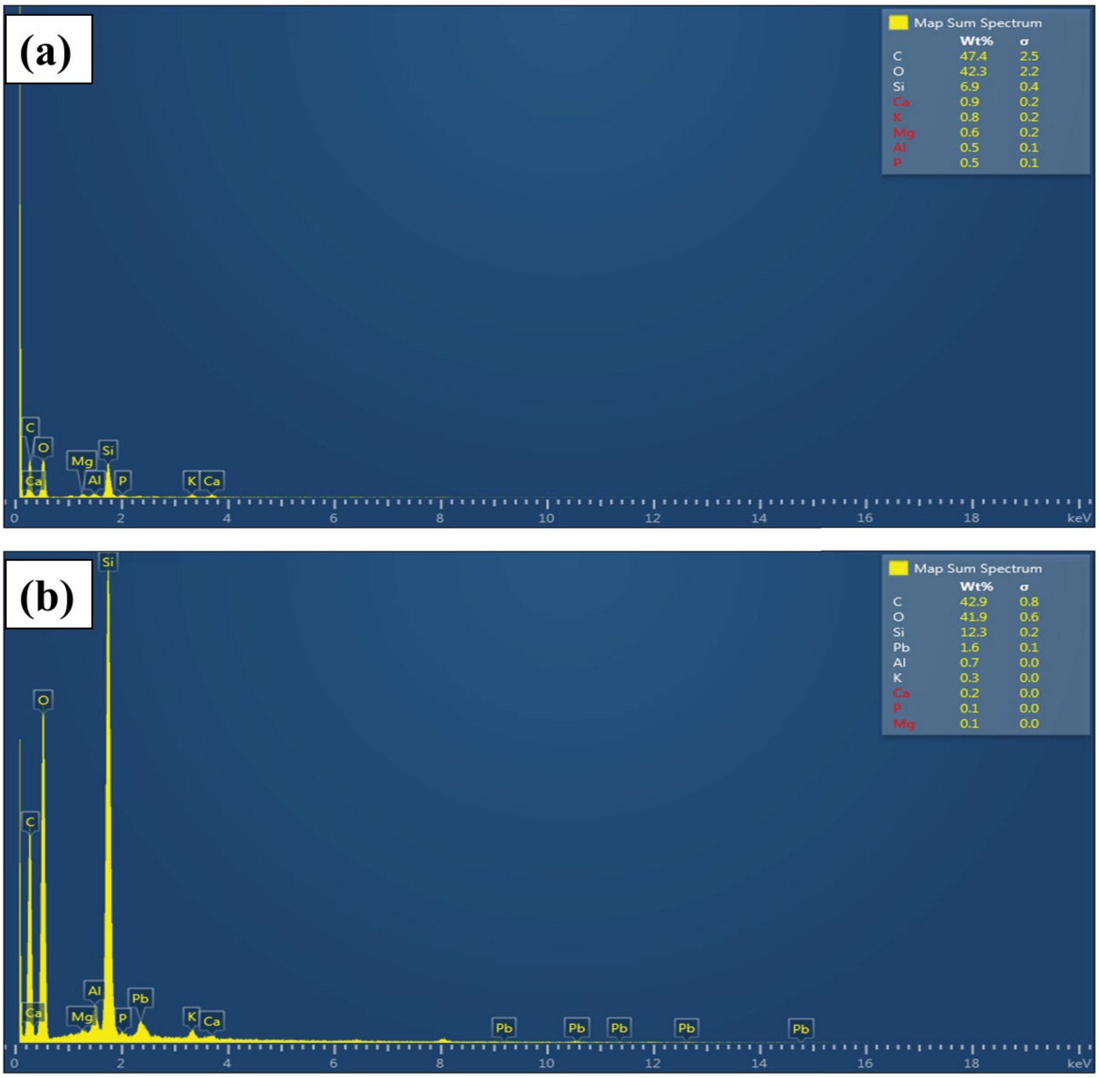


Fig. 2. EDS analysis of MRH, (a) before adsorption and (b) after lead ions removal.

same carbon, oxygen and silicon. Moreover, the lead (Pb) was detected on the MRH after adsorption, the weight percentage was about 1.6 wt.% confirming the successful removal of lead ions by the MRH.

### 3.2. FTIR analysis

In this study, FTIR spectroscopy was employed to prove adsorption of lead ions from aqueous solution onto MRH. FTIR spectrum of MRH before adsorption is illustrated in Fig. 3. The peak at 3,400–3,200 cm$^{-1}$ was associated to the surface O–H stretching, whereas aliphatic C–H stretching had a broad band at 2,921–2,851 cm$^{-1}$. The peaks at 1,217.0; 1,365.4; 1,737.8 and 1,027.4 cm$^{-1}$ were because of carboxyl group on MRH in the range of reported peaks at 1,208–1,230, 1,367–1,371, 1,740 and 1,029 cm$^{-1}$ for carboxyl group [68,69]. The peaks at 1,737.8; 1,435.6 and 1,365.4 cm$^{-1}$ were attributed to C=O stretching, O–H bending of the adsorbed $H_2O$ and aliphatic C–H bending, respectively [70]. Except, the peak at 1,074.0 cm$^{-1}$ coincides to anti-symmetric stretching vibration of Si–O, whereas at 476.2 cm$^{-1}$ showed the bending vibration of Si–O–Si bond [68,71,72]. The peaks related to non-conjugated carbonyl functional groups in the MRH spectrum showed hydrolyses of carbonyl groups during NaOH treatment.

After adsorption of lead ions from aqueous solution onto MRH, the changes in the spectrum of lead ions load MRH were noted (Fig. 3). There were slight shift of 1,739.4 and 1,367.3 cm$^{-1}$ peak of carbonyl, carboxyl functional groups and decline in their intensities were observed. A shift of ~12 and 11 cm$^{-1}$ was seen in 1,217.0 and 1,029 cm$^{-1}$ peaks. It showed the involvement of these functional groups into lead ions adsorption onto MRH.

### 3.3. Effect of operating factors on percentage removal of lead ions from aqueous solution by MRH

Fig. 4a denotes the influence of contact time on the percentage removal of lead ions from aqueous solution by using MRH under applied experimental conditions. It was noted that the percentage removal of lead ions from water was increased with contact time. For instance, the removal efficiency enhanced from 29% to 89% with increasing the contact time from 1 to 1,440 min. Initially, the removal of lead ions was rapid as shown in Fig. 4a. It is associated to the present of a lot of empty sites onto MRH. Therefore, the interaction between metal ions and MRH were developed and hence fast adsorption of lead ions onto it was observed. Then, the increase in the percentage removal of metal ions was very small. After that, the equilibrium was attained. There were no more enhancements in the removal of metal ions with contact time. Due to movement of lead ions into interior pores of MRH, the percentage removal was slowed down when all surface sites MRH (adsorbent) were saturated. Similar was observed in our previous work [73].

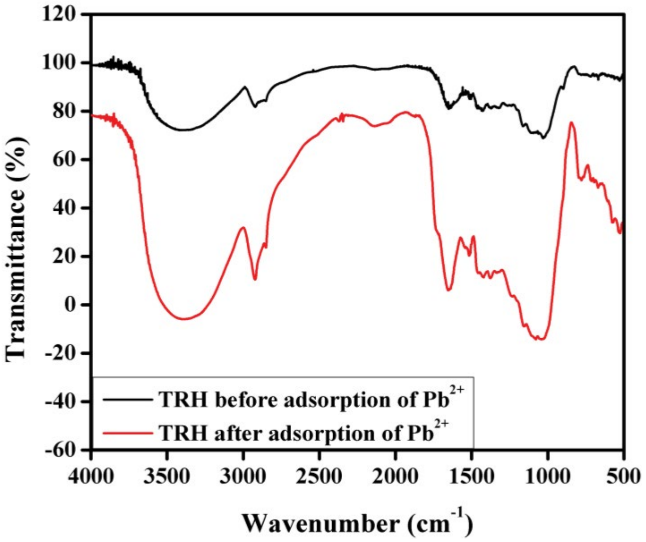


Fig. 3. FTIR spectrum of MRH before and after lead ions adsorption from aqueous solution.

The influence of adsorbent dosage toward a certain pollutant is an important parameter since it is required for the scale up of the utilization of an adsorbent in real applications. Fig. 4b represents the effect of the MRH-dosage onto the percentage removal of lead ions from aqueous solution. The results deomnstrated an increase in the removal efficiency with MRH dosage which is similar to our previous research [50,51,55]. For example, the removal efficiency found to increase from 44% to 98% with increasing MRH dosage from 0.010 to 0.040 g. The increase in the removal efficiency with adsorbent dosage is attributed to the increase of vacant adsorption sites associated with the adsorbent dosage against a fixed concentration of lead ions. The removal efficiency was more than 91% using 25 mg of MRH, further increasing the dosage resulted in increased

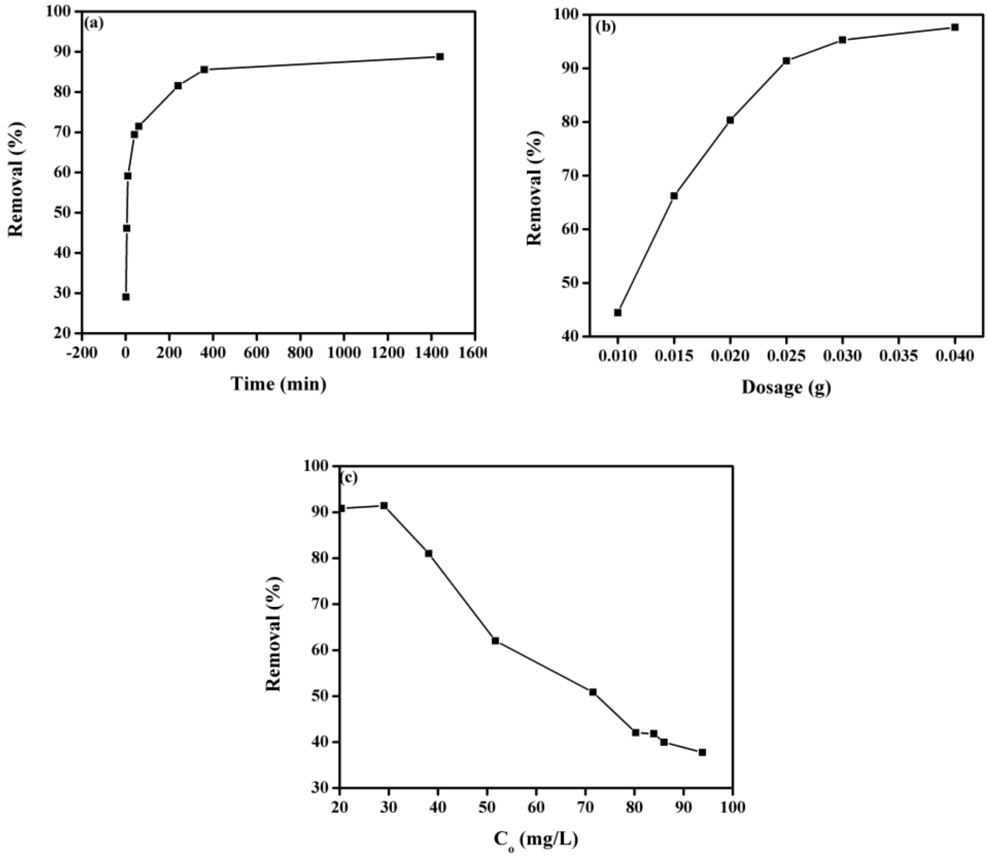


Fig. 4. (a) Effect of contact time, (b) dosage, and (c) initial concentration of lead ions solution on the percentage removal of lead ions from aqueous solution by MRH.

removal by 3%, hence the dosage of 25 mg was selected as an optimum dose and used for the rest of the study. Similar results were noted in our previous work [74].

The effect of initial concentration of lead ions onto the removal efficiency of lead ions was also considered and results are displayed in Fig. 4c. It was seen that; the removal efficiency was decreased from 91% to 27% with increasing initial concentration of metal ions aqueous solution. This was attributed to the saturation of adsorption sites onto MRH, some of metal ion was left unabsorbed at higher initial concentration. Also at low initial concentration, more binding spaces were presented resulting in higher removal efficiency. However, the number of competing metal ions for existing binding sites was enhanced with increasing initial concentration of metal ions. Similar results were noted in our previous work [44,45,53].

Temperature also has significant influence on adsorption of heavy metal ions from aqueous solution. Fig. 5a depicts the influence of temperature on the percentage removal of lead ions from aqueous solution by using MRH. Results showed that the removal lead ions was decreased from 89% to 85% with rise in temperature from 295 to 333 K. This trend it attributed to the decline in surface activity with rise temperature [44,75]. Moreover, increasing the temperature will increase the mobility of lead ions which in turn increase the kinetic energy of the lead molecules allowing them to escape from the adsorption sites and remain suspended in the bulk solution. Therefore, adsorption of lead ions onto MRH was exothermic process.

Fig. 5b represents effect of initial solution pH on the removal of lead ions from aqueous solution by using MRH. Solution acidity/basicity is an important parameter in adsorption studies since pH is not only influence the adsorbent charge but it also affects the precipitation of lead ions. Fig. 6 illustrates the zero point of charge ($pH_{ZPC}$) of the MRH and it was found to be 3.9. From Fig. 5b, it is observed that the removal of lead ions was found to be increased with initial solution pH from 2.6 to 5.5. Next, the removal efficiency was decreasing by increasing the solution pH to 6.8, which is mainly attributed to the lead ions precipitation. Further increasing the solution pH to basic conditions, the lead ions found to precipitate and hence basic conditions were not considered in the results. The maximum removal of lead ions from aqueous solution by MRH was attained at pH of 5.50 (acidic medium). The increase in lead ions removal with pH is attributed to the surface charge of the adsorbent. At pH 2.7, the adsorbent is positively charged and the removal efficiency is low due to the repulsive interactions with positively charged lead ions. Increasing the pH to 3.6, the removal efficiency increased to the reduction in the positive charge of the adsorbent which in turn reduce the magnitude of the repulsive interactions and hence the removal efficiency increased to 45%. After that (i.e., at pH > $pH_{ZPC}$), the adsorbent is positively charged and the adsorption is occurring due to the electrostatic interactions and hence improved adsorption capacity at pH 4.2 and 5.4. However, the removal efficiency

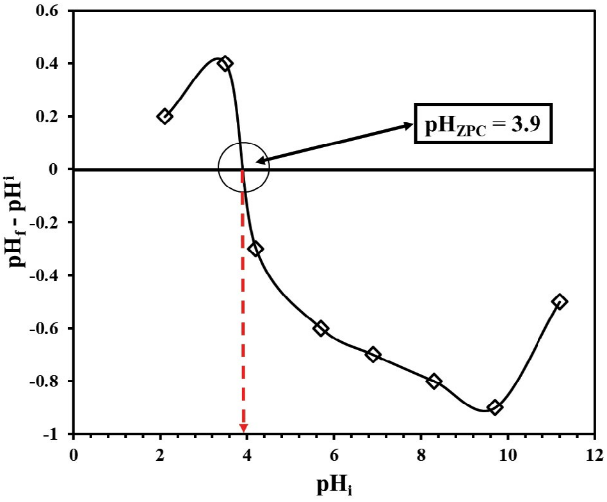


Fig. 6. Zero point of charge ($pH_{ZPC}$) of MRH by the pH drift method.

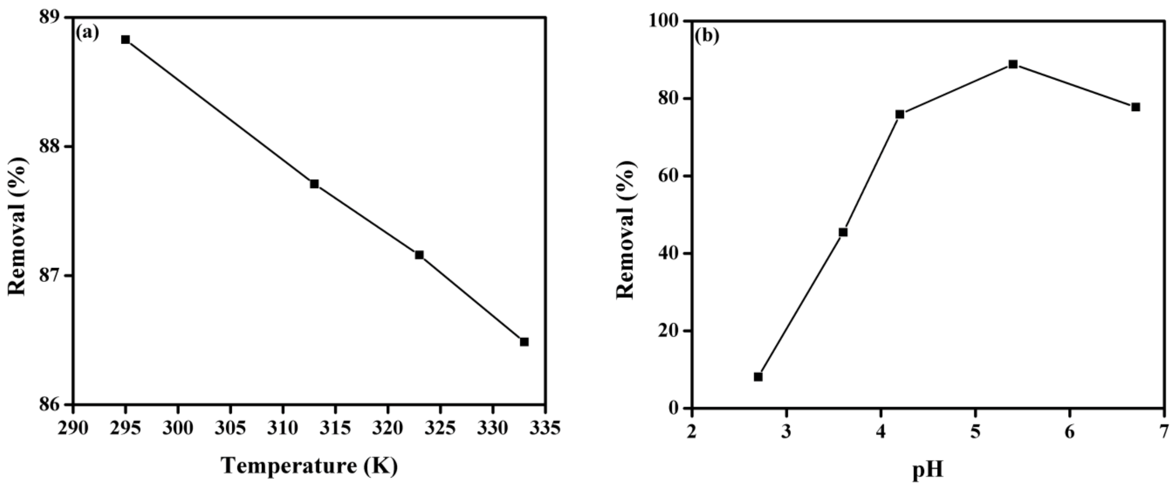


Fig. 5. (a) Effect of contact time, (b) dosage, and (c) initial concentration of lead ions solution on the percentage removal of lead ions from aqueous solution by MRH.

then decreased at pH 6.7 which is attributed to the precipitation of lead ions as mentioned above. These findings are consistent with the adsorption of silver ion from aqueous solution onto rice husk as reported in our previous work [56].

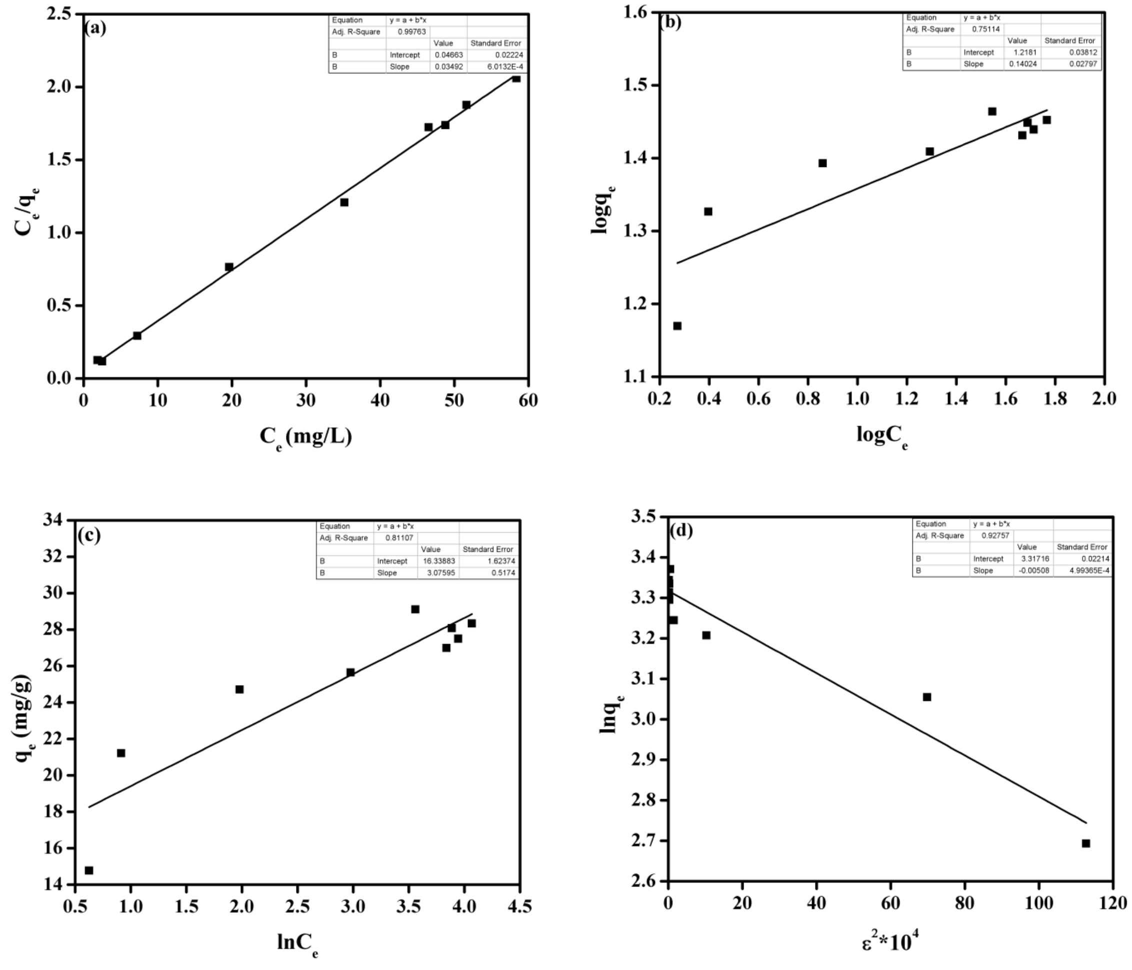
### *3.4. Adsorption isotherms*

Experimental data for lead ions adsorption onto MRH was subjected to Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms. Langmuir adsorption isotherm for lead ions adsorption onto MRH is represented in Fig. 7a and the determined values of its factors are given in Table 2. The correlation coefficient ($R^2 = 0.997$) value was close to unity which represented that lead ions adsorption onto modified-RH fitted well to Langmuir isotherm. Moreover, the calculated value of $R_L$ (0.014–0.062) denoted that lead ions adsorption onto MRH was favorable process. The plot of Freundlich isotherm for lead ions adsorption is depicted in Fig. 7b and the determined values of its factors are shown in Table 2. The value of correlation coefficient ($R^2 = 0.751$) represented that lead ions adsorption cannot be described by the Freundlich isotherm.

Table 2
Calculated values of isotherm parameters for lead ions adsorption from aqueous solution onto MRH

| Adsorption isotherms | Parameters | |
|---|---|---|
| | $Q_m$ | 28.63 |
| Langmuir isotherm | $K_L$ | 0.75 |
| | $R_L$ | 0.014–0.062 |
| | $R^2$ | 0.997 |
| | $n$ | 7.14 |
| Freundlich isotherm | $K_f$ | 16.52 |
| | $R^2$ | 0.751 |
| | $b_T$ | 799 |
| Temkin isotherm | $A_T$ | 194 |
| | $R^2$ | 0.811 |
| | β | $5 \times 10^{-3}$ |
| | $C_m$ | 27.58 |
| Dubinin–Radushkevich isotherm | $R^2$ | 0.928 |
| | $E$ | 10.0 |

$Q_m$ (mol/g); $K_L$ (L/mol); $K_f$ ((mg/g)(L/mg)$^{1/n}$); $C_m$ (mol/g); β (mol²/J²); $E$ (kJ/mol)



(a)

| Equation | y = a + b*x | | |
|---|---|---|---|
| Adj. R-Square | 0.99763 | | |
| | | Value | Standard Error |
| B | Intercept | 0.04663 | 0.02224 |
| B | Slope | 0.03492 | 6.0132E-4 |

(b)

| Equation | y = a + b*x | | |
|---|---|---|---|
| Adj. R-Square | 0.75114 | | |
| | | Value | Standard Error |
| B | Intercept | 1.2181 | 0.03812 |
| B | Slope | 0.14024 | 0.02797 |

(c)

| Equation | y = a + b*x | | |
|---|---|---|---|
| Adj. R-Square | 0.81107 | | |
| | | Value | Standard Error |
| B | Intercept | 16.33883 | 1.62374 |
| B | Slope | 3.07595 | 0.5174 |

(d)

| Equation | y = a + b*x | | |
|---|---|---|---|
| Adj. R-Square | 0.92757 | | |
| | | Value | Standard Error |
| B | Intercept | 3.31716 | 0.02214 |
| B | Slope | -0.00508 | 4.99365E-4 |

Fig. 7. (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin–Radushkevich isotherm for lead ions adsorption onto MRH.

Fig. 7c shows the plot of Temkin isotherm for lead ions adsorption onto MRH and the calculated values of $b_T$ and $A_T$ are shown Table 2. For this isotherm, the value of correlation coefficient ($R^2$ = 0.811) was smaller than Langmuir isotherm suggesting that lead ions adsorption onto MRH not followed Temkin isotherm. Dubinin–Radushkevich isotherm for lead ions adsorption onto MRH is shown in Fig. 7d and the values of Dubinin–Radushkevich constant ($C_m$) and are given in Table 2. The $R^2$ value of Dubinin–Radushkevich model is 0.927 implying that the isotherm data in good agreement with this model. For lead ions adsorption onto MRH, the calculated value mean adsorption energy was 10.0 kJ/mol. It exhibited that lead ions adsorption was chemical adsorption process. Similar was reported in our previous work [50,51,63]. The maximum Langmuir adsorption capacity was found 28.6 mg/g. This capacity found to be higher than raw rice husk and rice husk biochar. Table 3 presents the maximum Langmuir adsorption capacity of raw rice husk and carbon based materials obtained from rice husks.

### *3.5. Adsorption kinetics for lead ions adsorption onto MRH*

Herein, adsorption kinetics for lead ions adsorption from aqueous solution onto MRH was explored by applying several kinetics models. Fig. 8a illustrates the plot of pseudo-first-order model for lead ions adsorption onto MRH and its measured parameters ($K_1$ and $q_e$) are given in Table 4. It was noted that the value of correlation coefficient ($R^2$) was 0.895. There was a large difference between calculated adsorption capacity values ($q_{e,\text{cal}}$ = 8.29 mg/g) and experimental adsorption capacity ($q_{e,\text{exp}}$ = 20.30 mg/g). Hence, the rate process can't be explained by pseudo-first-order model. The plot of pseudo-second-order model is represented in Fig. 8b and the calculated factors for

Table 3
Adsorption capacities of lead onto rice husks and carbonaceous materials derived from rice husk

| Adsorbent | Maximum adsorption capacity | References |
|---|---|---|
| NaOH-modified rice husk | 28.6 | This study |
| Raw rice husk | 4.0 | [33] |
| Rice husk ash | 91.74 | [34] |
| Rice husk biochar | 26.7 | [35] |
| NaOH-treated rice husk activated carbon | 49.2 | [76] |

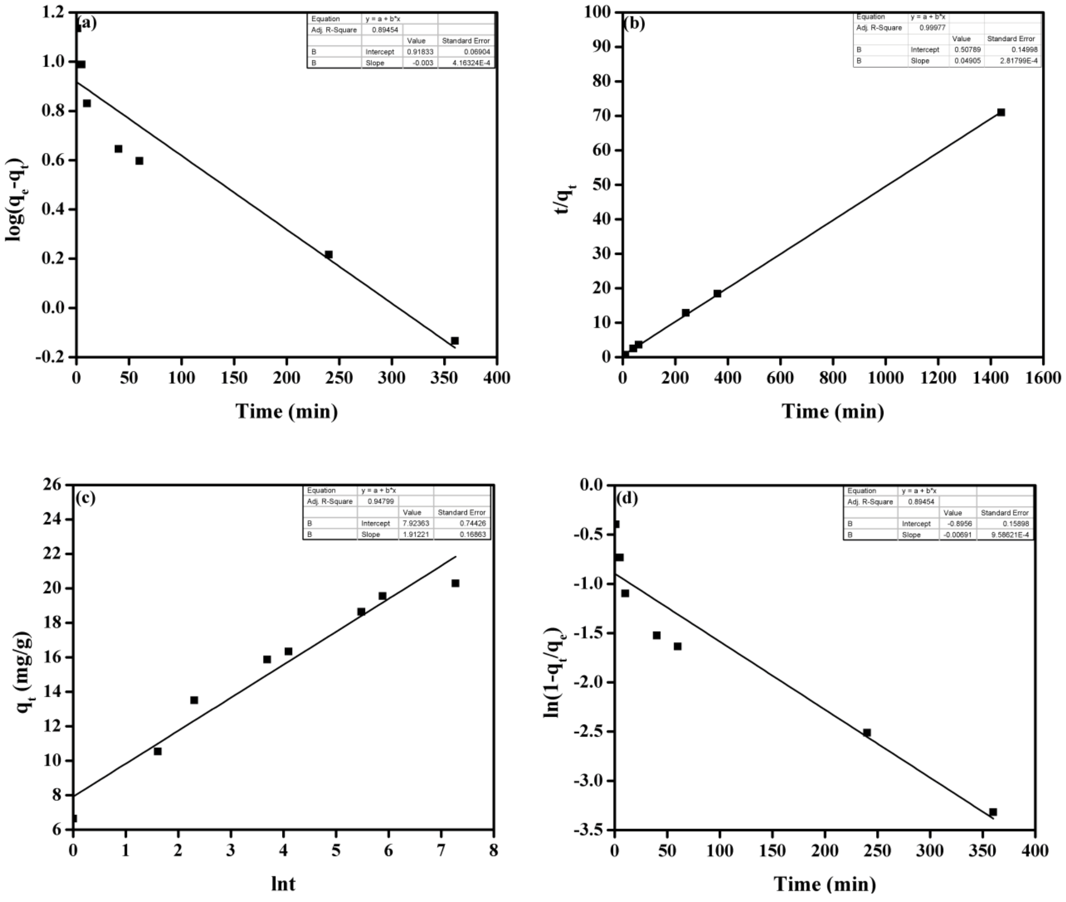


Fig. 8. (a) Pseudo-first-order model, (b) pseudo-second-order model, (c) Elovich model, and (d) liquid film diffusion model for lead ions adsorption onto MRH.

Table 4
Measured parameters of adsorption kinetic models for lead ions adsorption onto MRH

| Kinetic models | Parameters | |
|---|---|---|
| Pseudo-first-order model | $q_{e,\mathrm{exp}}$ | 20.30 |
| | $q_{e,\mathrm{cal}}$ | 8.29 |
| | $K_1 \times 10^{-3}$ | 3.0 |
| | $R^2$ | 0.895 |
| Pseudo-second-order model | $q_e$ | 20.40 |
| | $K_2 \times 10^{-3}$ | 4.71 |
| | $R^2$ | 0.999 |
| Elovich model | $\alpha$ | 0.52 |
| | $\beta$ | 118.36 |
| | $R^2$ | 0.974 |
| Liquid film diffusion model | $K_{\mathrm{fd}} \times 10^{-3}$ | 6.91 |
| | $C_{\mathrm{fd}}$ | –0.89 |
| | $R^2$ | 0.895 |
| Modified Freundlich equation | $m$ | 6.67 |
| | $k$ | 0.27 |
| | $R^2$ | 0.862 |
| Bangham equation | $k_o$ | 8.23 |
| | $\alpha$ | 0.15 |
| | $R^2$ | 0.862 |

$q_e$ (mg/g); $K_1$ (min$^{-1}$); $K_2$ (g/mg min); $\alpha$ (mg/g min); $\beta$ (g/mg); $K_{\mathrm{fd}}$ (min$^{-1}$); $k$ (L/g min); $k_o$: (mL/g/L)

it are shown in Table 4. From here, it was seen that the value of experimental ($q_{e,\mathrm{exp}}$ = 20.30 mg/g) and calculated adsorption capacity ($q_{e,\mathrm{cal}}$ = 20.40 mg/g) were very close to each other. In addition, the value of correlation coefficient was close to unity ($R^2 > 0.999$) representing that lead ions adsorption onto MRH followed pseudo-second-order model. The plot of Elovich model for lead ions adsorption onto MRH is denoted in Fig. 8c and its calculated factors ($\alpha$ and $\beta$) are given in Table 4. As it can be seen from this Table 4, the value of correlation coefficient ($R^2$ = 0.974) was smaller than pseudo-second-order model. Fig. 8d indicates liquid film diffusion model's plot for lead ions adsorption onto MRH and the determined values of its endowments are given in Table 4. For liquid film diffusion model, the value of correlation coefficient ($R^2$ = 0.895) was also smaller than pseudo-second-order model exhibiting that it was not good to study adsorption of lead ions from aqueous solution onto MRH.

For lead ions adsorption from aqueous solution onto MRH, the modified Freundlich equation plot is shown in Fig. 9a and the corresponding parameters are presented in Table 3. The determined value of correlation coefficient ($R^2$ = 0.862) was smaller than pseudo-second-order model. It revealed that the experimental data was not fitted to modified Freundlich equation. Fig. 9b represents the plot of Bangham equation plot for lead ions adsorption of onto MRH and the measured values of endowment ($\alpha$ and $m$) are represented in Table 4. For lead ions adsorption onto MRH, the double logarithmic plot did not give linear curve indicating that the diffusion of adsorbate (lead ions) into pores of the adsorbent (MRH) is not the only rate controlling step [50,63]. For lead ions adsorption from aqueous solution by MRH, it might be that both film and pore diffusion crucial to different extent.

### 3.5.1. Intraparticle diffusion study

To further investigate the adsorption mechanism of Pb(II) ions onto MRH, the intraparticle diffusion model was applied on the kinetic data. Intraparticle diffusion model is usually applied to study the rate limiting step of the adsorption process. The intraparticle diffusion is given in the following equation:

$$q_t = k_{\mathrm{ip}}\sqrt{t} + c \tag{19}$$

where $q_t$ is the adsorption amount at time (t), $k_{\mathrm{ip}}$ (mg/(g min$^{1/2}$)) is the constant of the intraparticle diffusion model, and $c$ (mg/g) is the intercept of the model. By plotting the data $q_t$ against the square root of time, if the data points fit a straight line and passes through the origin, then the intraparticle diffusion is the controlling adsorption mechanism. Otherwise, several limiting steps are controlling the adsorption process. As depicted in Fig. 10, the data points didn't form one straight line and didn't cross the origin and hence the intraparticle diffusion is not controlling the adsorption process and the surface film diffusion significantly influence the adsorption process. By splitting the intra-particle points into three segments, 3 straight lines were observed with a correlation factors ($R^2$) for the trend lines between 0.999 and 1. Step 1 belongs to the surface film diffusion, this step occurred in short time (around 10 min) and found to be responsible of 66.6% of the total adsorption capacity. Next, Step 2 belongs to the pore diffusion of Pb(II) ions in the internal surface of the MRH. Step 2 found to monitor 29.8% of the total adsorption capacity, this step is a slow adsorption process and achieved in 350 min. The last step (step 3), belongs to the equilibrium state where the Pb(II) adsorbed on the mesoporous structure of the adsorbent and the remaining vacant sites on the adsorbent surface, this step is responsible of 3.6% of the total adsorption capacity. To conclude, the adsorption of Pb(II) ions by MRH is mainly controlled by surface adsorption and to a lesser extent the pore diffusion in the internal pores of the adsorbent.

Based on the isotherm, kinetics, influence of pH and FTIR results, Fig. 11 illustrates the possible interactions of lead ions onto the surface of MRH. It can be summarized that both physical and chemical adsorption processes going on, the electrostatic interactions, surface and pore diffusion were also affected the removal process.

### 3.6. Adsorption thermodynamics for lead ions adsorption from aqueous solution onto MRH

To study the thermodynamics of lead ions adsorption from aqueous solution by MRH, the values of change Gibb's free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were measured. The plot of ln$K_c$ vs. $1/T$ for lead ions adsorption onto MRH is represented in Fig. 8c and the calculated values of thermodynamic factors ($\Delta G°$, $\Delta H°$, $\Delta S°$) are given

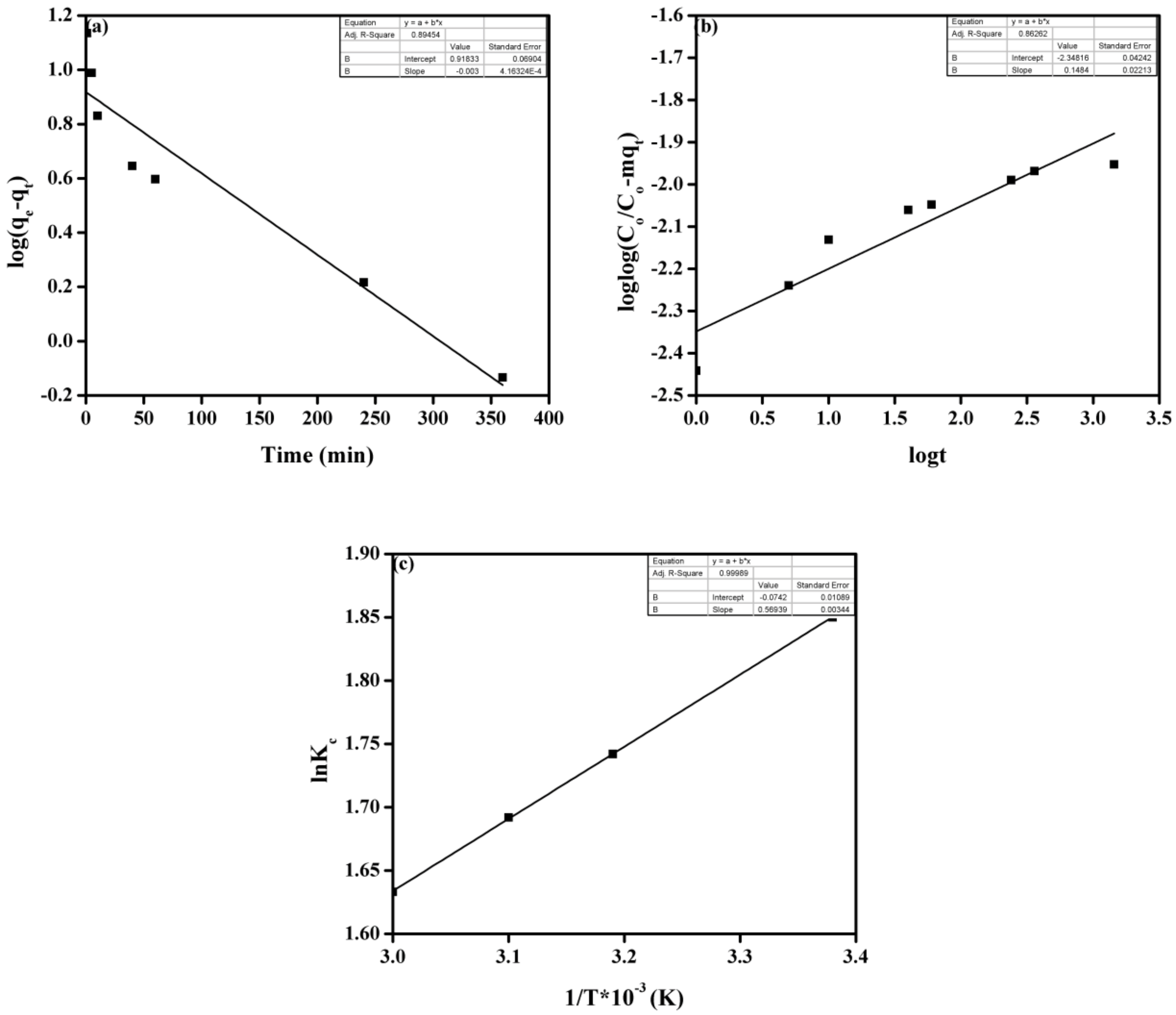


Fig. 9. (a) Modifies Freundlich equation, (b) Bangham equation, and (c) the plot of $1/T$ vs. $\ln K_c$ for adsorption of lead ions from aqueous solution onto MRH.

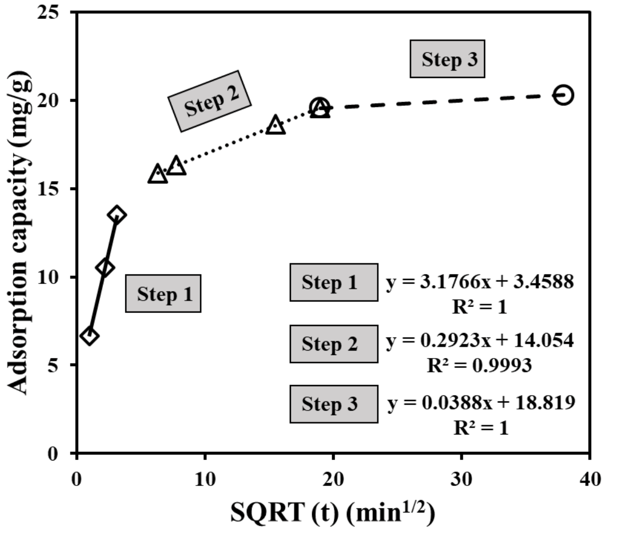


Fig. 10. Intraparticle diffusion study of lead ions removal by MRH.

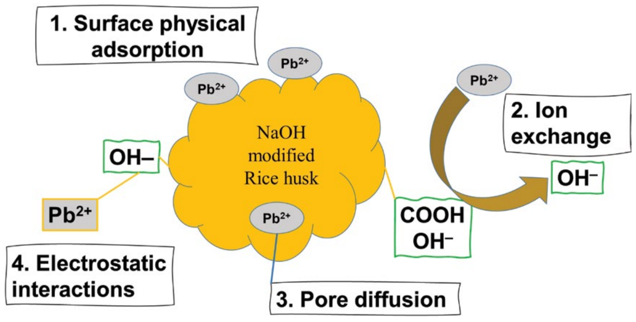


Fig. 11. Possible adsorption mechanisms/interactions of lead ions removal by modified rice husks.

in Table 5. The negative value of enthalpy ($\Delta H°$) represented that adsorption of lead ions was an exothermic process. Moreover, the negative value of entropy ($\Delta S°$) during lead ions adsorption onto MRH indicated decreases in the degree of randomness at the adsorbent–adsorbate interface. The negative value of Gibb's free energy showed that

Table 5
Measured thermodynamic factors for adsorption of lead ions from aqueous solution onto MRH

| Temperature (K) | Δ*H* (kJ/mol) | Δ*S* (J/K mol) | Δ*G* (kJ/mol) |
|---|---|---|---|
| 295 | –4.61 | –0.25 | –4.537 |
| 313 | | | –4.533 |
| 323 | | | –4.544 |
| 333 | | | –4.522 |

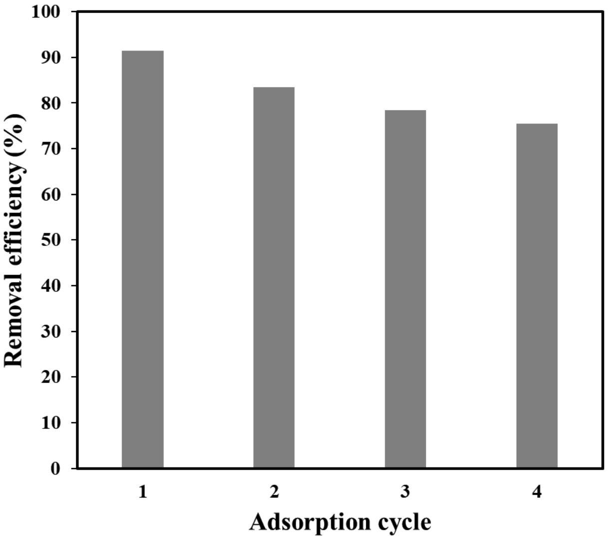


Fig. 12. Removal efficiency of lead ions against the adsorption/desorption cycles.

adsorption process was spontaneous in nature. The increase in values of Gibb's free energy with rise in temperature represented that the adsorption process is favored at room temperature than at higher temperatures.

### 3.7. Regeneration experiments

Desorption and regeneration experiments are very important to evaluate the reusability of MRH for lead ions removal. Therefore, the MRH were tested for the removal of lead ions in 4 adsorption/desorption cycles. Desorption was conducted by washing the spent adsorbent with 0.1 M HCl solution and the results are illustrated in Fig. 12. The MRH demonstrated a relative decrease in the removal efficiency of lead ions with adsorption/desorption cycles. However, more than 75% of an initial concentration of 30 mg/L of lead ions can still be achieved after 4 adsorption/desorption cycles. These results suggesting that MRH can be utilized for the remediation of lead ions from aqueous solution s.

## 4. Conclusions

In this manuscript, lead ions adsorption from aqueous solution onto MRH was investigated in detail. FTIR spectroscopy showed adsorption of lead ions onto MRH. The percentage removal of lead ions was enhanced with contact time, mass of MRH, pH while deceased with initial concentration of lead ions in aqueous solution and temperature. Adsorption isotherm study represented that adsorption of lead ions onto MRH fitted to Langmuir isotherm. Kinetics study showed that lead ions adsorption fitted to pseudo-second-order model. It was found that the adsorption was mainly controlled by surface film diffusion and in less extent by pore diffusion. Thermodynamics evaluation indicated that lead ions adsorption onto MRH was exothermic and spontaneous process. The MRH demonstrated more than 75% removal of lead ions after 4 adsorption/desorption cycles. From this we concluded that MRH could be employed as an excellent adsorbent for removal of lead ions from aqueous solution.

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## Supplementary information

### S1. Reasons behind selecting the adsorption parameters

The influence of adsorption parameter was evaluated by batch mode adsorption experiments. The effect of the adsorption parameters was investigated by one parameter at a time, (i.e., varying one parameter and keeping other parameters constants). Unless stated otherwise, the adsorption experiments started by investigating the effect of adsorbent dosage on the removal of 30 mg/L. In this experiment, the left over concentration was measured after 24 h and at the same time the adsorption tests were left for 48 h to explore if there are any changes in the effluent concentration. The removal was constant and no major changes in the final concentrations. Next, the optimum dose (25 mg in 20 mL for the removal of an initial lead concentration of 30 mg/L), was repeated in order to see the effect of contact time. After that, using the optimum dose, the influence of the initial concentration (20–100 mg/L) was investigated. The highest concentration was selected to be 100 mg/L which is far enough to explore the maximum adsorption capacity as at higher concentrations, no major changes in the adsorption capacity were observed. For the effect of temperature, the experiments were carried out by varying the temperature between 295 and 333 K. According to temperature profiles of UAE, this range was selected as all water streams temperature available in this range. For the pH, it was inspected for pH 2.7 to 6.7, which is acidic to neutral conditions. Experiments at higher pH were conducted, but during preparation of lead solution, white precipitate was directly formed, moreover, the initial concentration of Pb(II) was far away from what we have prepared indicating the formation of lead hydroxides and hence the results were not considered in the manuscript.